Title	Single Crystal Growth at High Pressure (SOLID STATE CHEMISTRY-Multicomponent Materials)
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Citation	ICR annual report (2000), 6: 20-21
Issue Date	2000-03
URL	http://hdl.handle.net/2433/65239
Right	
Type	Article
Textversion	publisher

Single Crystal Growth at High Pressure

Masaki Azuma, Takashi Saito and Mikio Takano

Single crystals of a spin-1/2 Heisenberg alternating chain compound, high pressure phase of $(VO)_2P_2O_7$, was grown by slowly cooling the melt at 3 GPa. Powder XRD study at high pressure using synchrotron radiation was performed in advance to observe the formation and the melting of this compound.

Keywords: High pressure synthesis/ Synchrotron radiation XRD/ Single crystal growth

High pressure synthesis is a powerful technique to search for new materials. Various quantum spin compounds including high T_c superconductors and quantum spin ladders [1] have been found using this method in a past decade. However, the limitation of the sample space and the difficulty in the direct observation of high pressure reactions made it difficult to grow single crystals of such compounds.

The high pressure phase of $(VO)_2P_2O_7$ (HP-VOPO) is a spin-1/2 Heisenberg alternating chain compound with a spin gap stabilized at 2GPa and 700 °C[2]. We have succeeded in growing single crystals of this compound by slowly cooling the melt at 3GPa [3]. High pressure powder X-ray diffraction (XRD) was performed using a cubic-anvil type high pressure apparatus (SMAP 1800) installed at BT14B1 of SPring-8, Japan Synchrotron Radiation Research Institute, to determine the melting temperature. White beam X-ray from the synchrotron radiation was irradiated to the sample in a platinum capsule through the high pressure cell and was detected by the solid state detector fixed at $2\theta = 4°$. Figure 1 shows the XRD patterns taken at 3GPa and at various temperatures. When the pressure was applied, the peak shifted to the high energy direction indicating a shrinkage of the lattice. The peak broadening was due to strains in the particles. The peaks sharpened again with increasing the temperature and new peaks corresponding to (2 2 1), (1 1 3) and (2 3 1) reflections of the HP phase appeared at 500°C. This clearly showed that the transition to the HP phase took place between 400 and 500°C. Finally at 1150°C the sample melted and all the peaks disappeared expect for those of characteristic X-rays of lead.

Single crystals were grown by slowly cooing the melt at 3GPa. About 2 g of the ambient pressure phase sample was packed in a platinum capsule of 9.6 mm in diameter and 15 mm height and compressed using a cubic anvil type high pressure apparatus. The sample was first heated to 1200°C and then cooled to 600°C in 60 h. Green transparent crystals of a typical size of 1 mm × 0.5 mm × 0.2 mm were obtained. A magnified view of obtained crystals is shown in Fig. 2.

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SOLID STATE CHEMISTRY — Multicomponent Materials —

Scope of research

Novel 3d transition-metal oxides showing exotic electrical and magnetic properties are being searched for using different synthesizing techniques like high pressure syntesis (5 GPa and 1000℃, typically) and epitaxial film growth. Recent topics are:

- *High T_c superconductivity.*
- *Low-dimensional spin systems like ladders showing dramatic quantum effects.*
- *Oxides of late 3d transition metals like $SrFeO_3$ with strong oxygen-hole character.*

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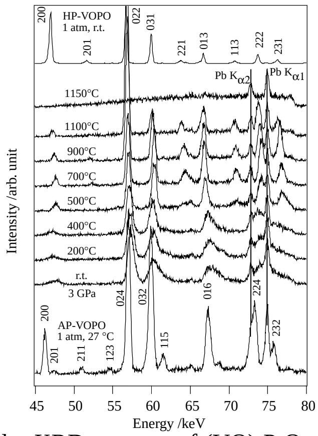

Figure 1 Powder XRD patterns of $(VO)_2P_2O_7$ taken at 3 GPa and various temperatures.

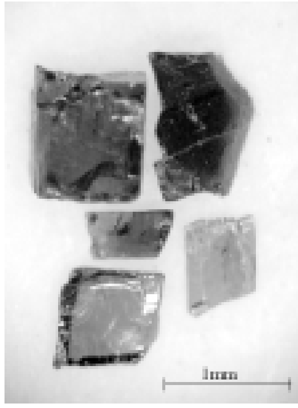

Figure 2 Single crystals of HP $(VO)_2P_2O_7$ grown at 3 GPa.

Epitaxial Growth of Fe^{4+}(3d^4)-Perovskite Oxides Thin Films

T. Terashima, N. Hayashi and M. Takano

Epitaxial films of $SrFeO_3$ containing high valent Fe^{4+}(3d^4) were successfully grown by the pulsed laser ablation and subsequent ozone annealing. The film showed good crystallinity and lower resistivity than a bulk sample.

Keywords: Fe^{4+}/ Perovskite oxides/ Thin film/ Epitaxial growth/ Laser ablation

Perovskite-type oxides containing high valent Fe^{4+}(3d^4) are prototypical systems to study electronic properties dominated by oxygen-hole character. $SrFeO_3$ (SFO) is a broad band metal down to the lowest temperature. Although the electronic state of SFO has attracted much attention, detailed transport properties have not been clarified due to the difficulty of the preparation of a single crystal. The high pressure treatment is required to oxidize Fe to Fe^{4+} state. The epitaxial growth is an alternative way to prepare a metastable substance. We report a successful growth of the epitaxial thin films of SFO by the pulsed laser deposition and subsequent ozone oxidation.

The films were grown by the pulsed laser deposition with KrF eximer laser (λ=248nm). The deposition conditions are the following: The substrate temperature was 650˚C and the oxygen pressure during the deposition was 500mTorr. The substrate was LSAT $((LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7})$ (100) which has a good lattice matching with SFO. After the deposition the film was cooled with blowing partially ozonized oxygen.

The epitaxial growth was confirmed by the reflection high-energy electron diffraction measurement. An equi-intensity contour map of X-ray scattering around (203) point for the SFO film is displayed in Fig.1. The narrow peak widths of the SFO film comparable to those of the substrate show good crystallinity of the film. The calculated in-plane and out-of plane lattice spacings are 3.865Å and 3.837Å, respectively, revealing a pseudo tetragonal structure of the film caused by an elastic strain.

Figure 2 shows the temperature dependence of the resistivity for the SFO film. The film exhibited metallic behavior with much lower resistivity than bulk sample prepared by high-pressure synthesis. A change in dR/dT is seen at 100K, which would be correlated to a magnetic ordering. Measurements of the transport properties, such as Hall effect and magnetoresistance, of the SFO film are now in progress.

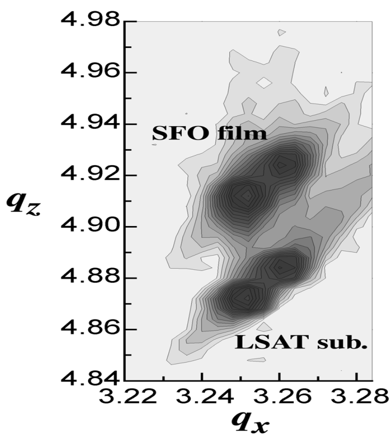

Figure 1. Equi-intensity contour map of X-ray scattering around the (203) point for the SFO thin film.

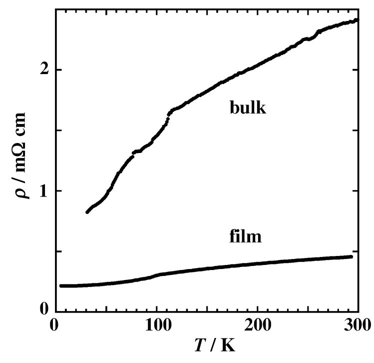

Figure 2. Temperature dependence of the resistivity for the SFO thin film and bulk.